STABILIZED SPINEL AND POLYANION CATHODES

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OVERVIEW

Timeline

- Project start date: January 2012
- Project end date: December 2015
- 25 % complete

Budget

- Total project funding
  - DOE: $1,120K
- Funding for FY12
  - $280K
- Funding for FY13
  - $280K

Barriers

- Barriers
  - Cost
  - Cycle life
  - Energy and power densities
- Targets
  - Long cycle-life high-voltage (4.7 V) spinel cathodes
  - High-capacity and high-voltage polyanion cathodes

Partners

- None officially

RELEVANCE

Project Objectives

- To develop high-performance spinel and polyanion cathodes for lithium-ion batteries and a fundamental understanding of their structure-composition-performance relationships

  - To develop high-voltage (4.7 V) spinel oxide cathodes with optimum surface morphologies/facets and cationic substitutions that can maximize the tap density, cycle life, energy, and power, while keeping the cost low

  - To develop novel low-cost, low-temperature synthesis processes to obtain high-capacity, nanostructured phosphate and silicate cathodes and their nanocomposites with graphene

  - To develop a fundamental understanding of the factors that control the electrochemical performances of high-voltage spinel and polyanion cathodes

MILESTONES

Month/Year	Milestone
June 2012	Surface characterization of $LiFe_{1-x}M_xPO_4$ (M = Mn and Co) with various x by XPS and ToF-SIMS
September 2012	Novel synthesis and characterization of Li_2MSiO_4 and the solid solutions
December 2012	Understanding the influence of morphology and crystal planes on the electrochemical performance of high-voltage spinels

APPROACH / STRATEGY

- Develop a firm understanding of the factors controlling the electrochemical performances of cathode materials and utilize the understanding to develop high-performance cathodes for vehicle batteries

- Synthesis optimization to stabilize various morphologies/facets of 4.7 V spinel
- Surface-plane control to improve electrochemical performances of 4.7 V spinel
- New methods to quantify degree of cation disorder in 4.7 V spinel cathodes
- Solution-based synthesis to obtain nanostructured phosphates and silicates
- Graphene integration into polyanion cathodes to improve electronic-ionic transport
- Microstructure optimization to reversibly extract > one Li per transition metal

- Solid-state, high-energy ball milling, and solution-based synthesis approaches
- Advanced chemical, structural, and surface characterizations
- In-depth electrochemical evaluation including impedance analysis
- Understanding the structure-property-performance relationships

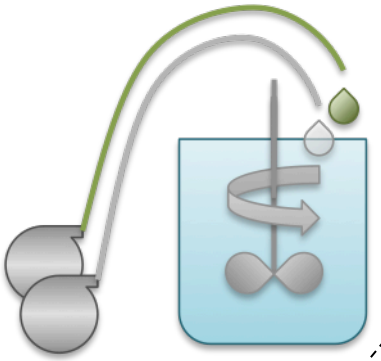
TECHNICAL ACCOMPLISHMENTS AND PROGRESS

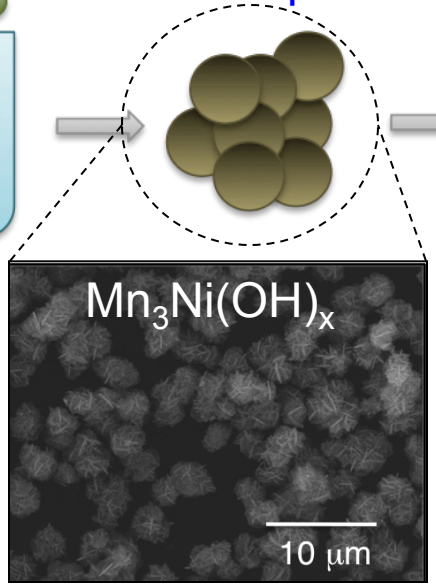
- The factors influencing the electrochemical properties of high-voltage (4.7 V) spinel cathodes have been systematically investigated
  - particle morphology/facets and surface planes play a dominant role compared to other factors like cation ordering on the electrochemical properties
  - novel synthesis methods have been developed to obtain various morphologies
  - two methods have been developed to determine relative degree of cation ordering
- Three polymorphs of $LiVOPO_4$ have been synthesized by a low-temperature synthesis approach in mixed solvents and have been shown to reversibly extract/insert more than one lithium per vanadium with a capacity of > 200 mAh/g
- $Li_3V_2(PO_4)_3$-supported on graphene has been synthesized by a solvothermal process and shown to exhibit capacities close to 200 mAh/g and high rate
- Li_2FeSiO_4-graphene nanocomposite has been synthesized by a microwave-assisted synthesis process and has been shown to reversibly extract/insert more than one lithium per Fe

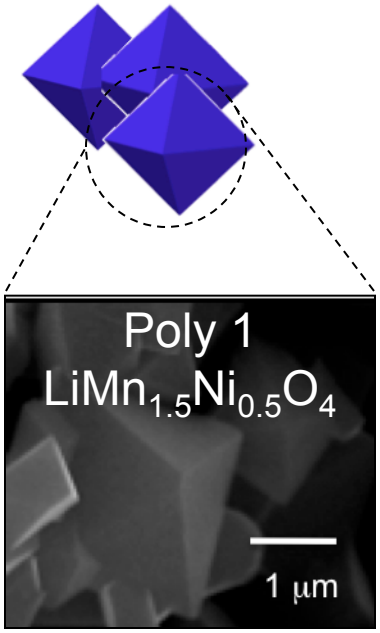
ROLE OF SYNTHESIS CONDITIONS ON 5 V SPINEL MORPHOLOGY

- Factors such as pH, temperature, and reaction time affect $M(OH)_x$ precursor
- Conditions can be modified to produce octahedral or truncated octahedral spinel

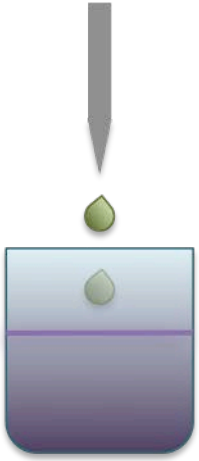
Polyhedral 1: Tank reactor, NH_3 complexing agent produces uniform precursor morphology

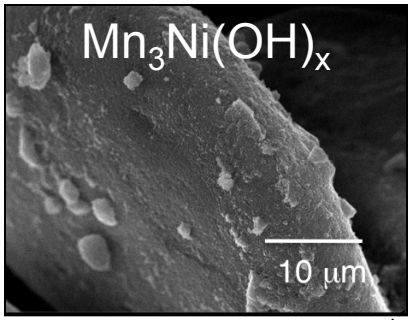


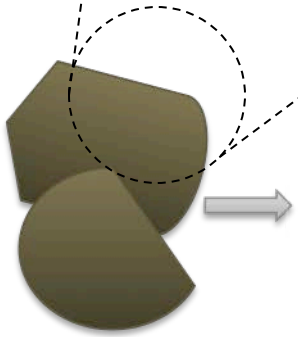


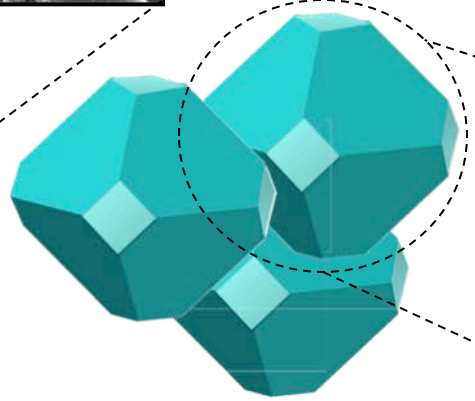


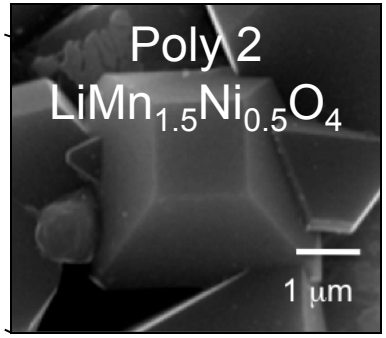
Polyhedral 2: Burette co-precipitation, precursor morphology is large and irregular



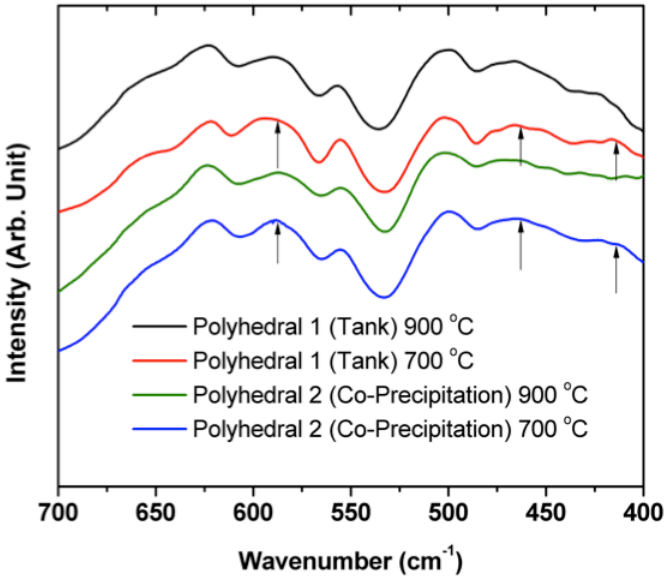


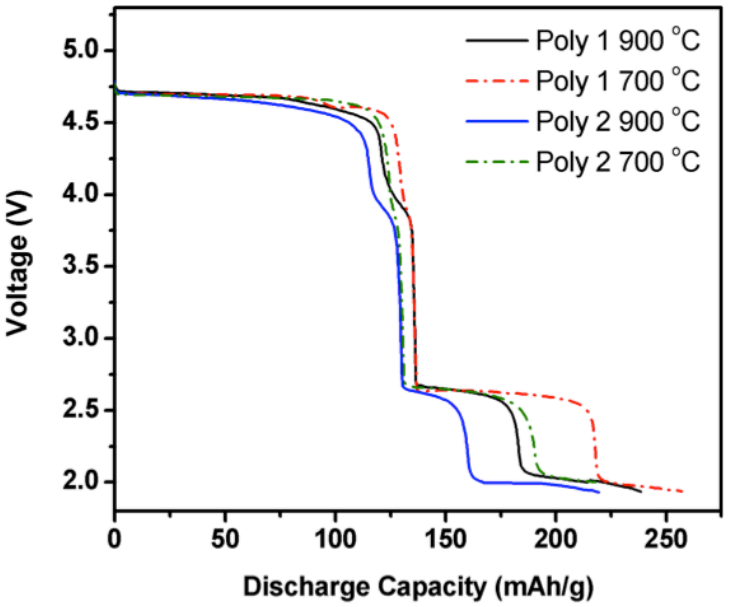


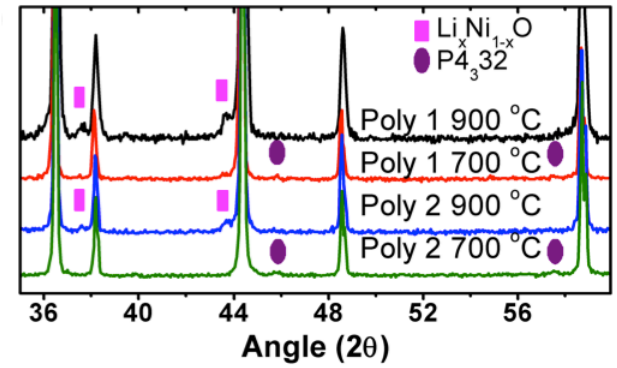


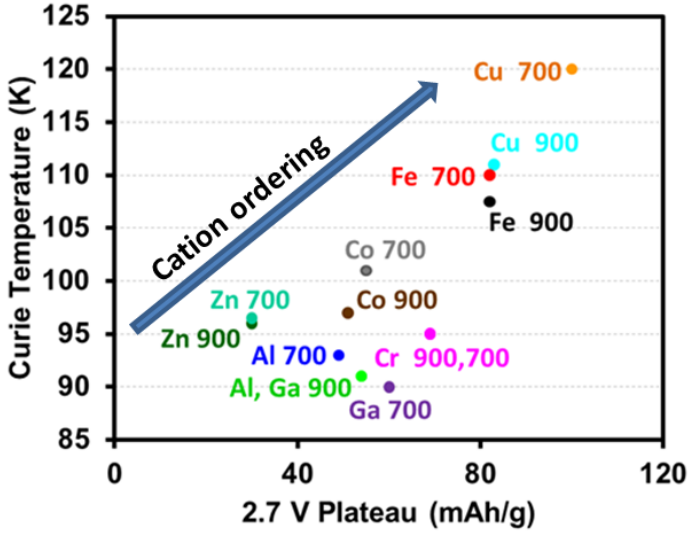


DEGREE OF CATION ORDERING IN 5 V SPINEL



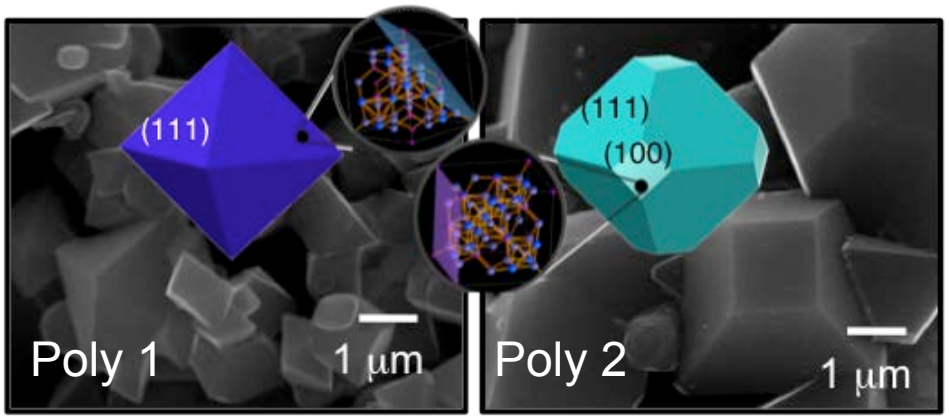






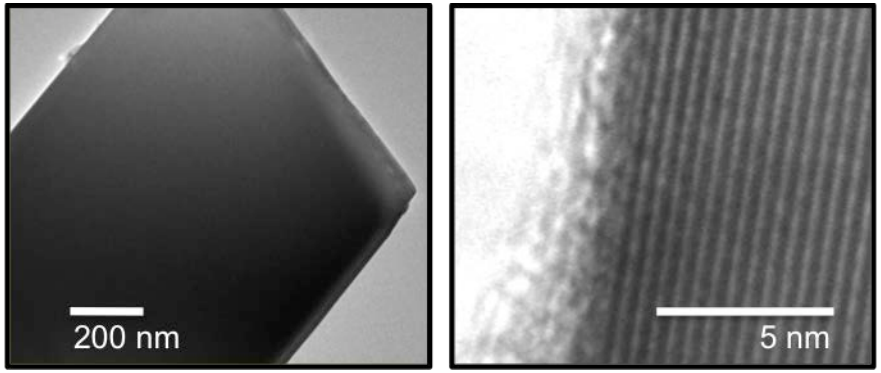
- Discharge below 3 V and magnetic data (new methods developed) indicate increase in cation ordering on annealing at 700 °C

TEM ANALYSIS OF CRYSTALLOGRAPHIC PLANES

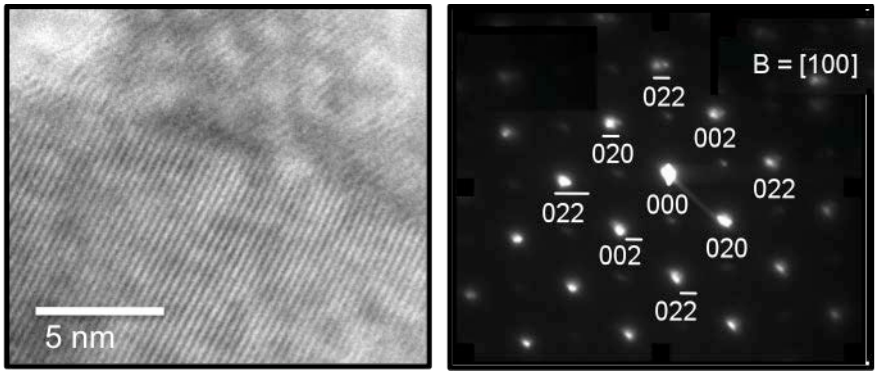


- Octahedral Poly 1 sample has uniform morphology with {111} family of planes on the surface
- Truncated Poly 2 sample has a mixture of (111) and (100) planes on the surface
- (100) plane has higher surface energy, forms a thicker SEI layer, and has a higher rate of Mn dissolution than the (111) plane

Poly 1: HR-TEM lattice fringe analysis confirms (111) planes

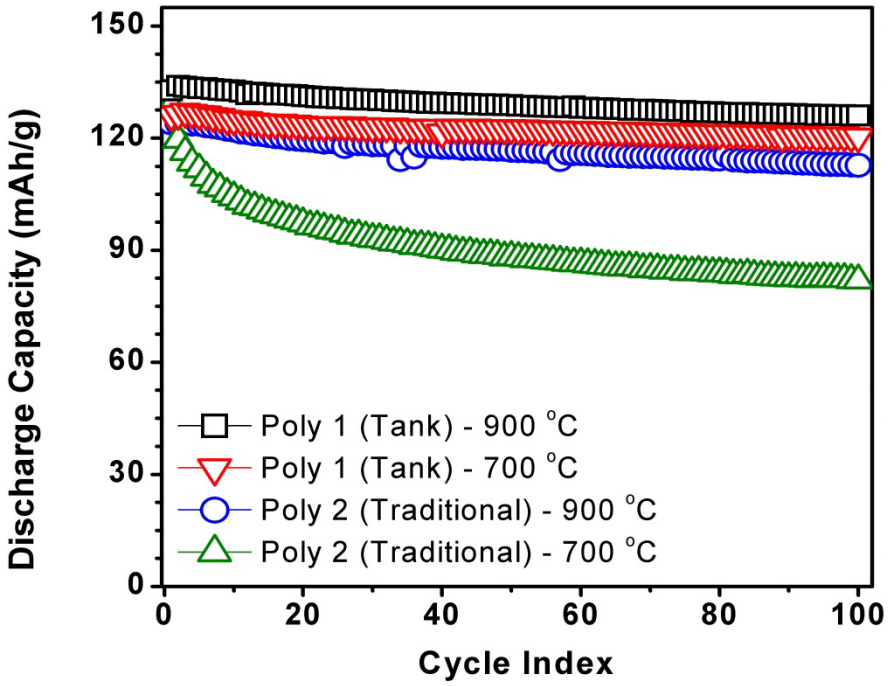


Poly 2: HR-TEM and electron diffraction confirm (111) and (100) planes

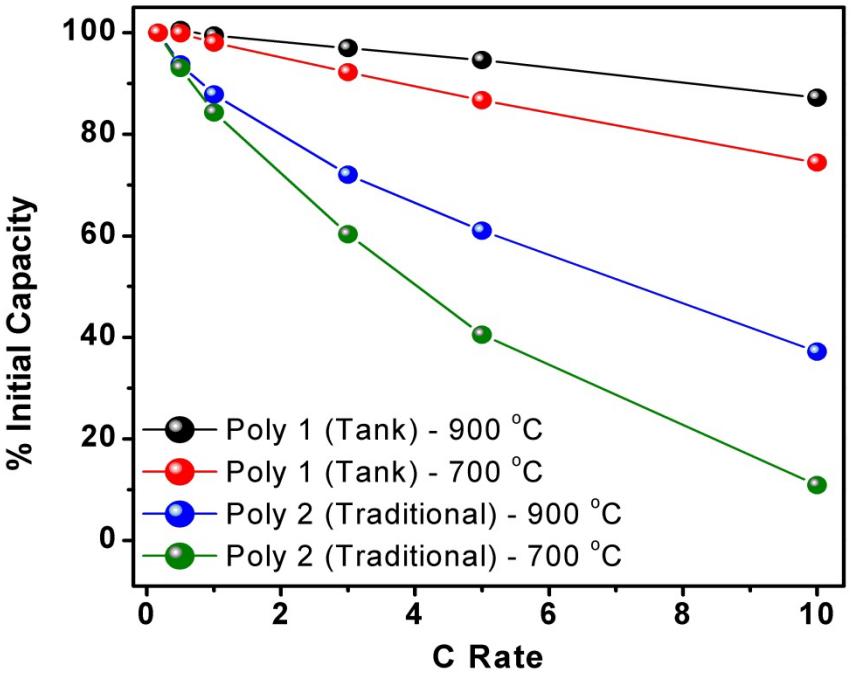


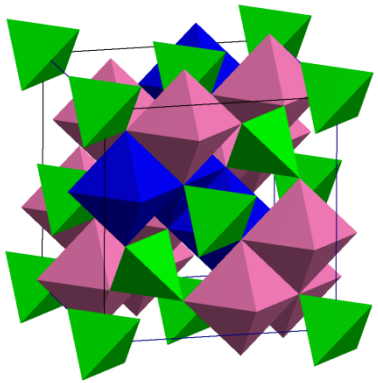
ROLE OF MORPHOLOGY ON ELECTROCHEMICAL PROPERTIES

Cyclability at C/6 rate



Rate capability

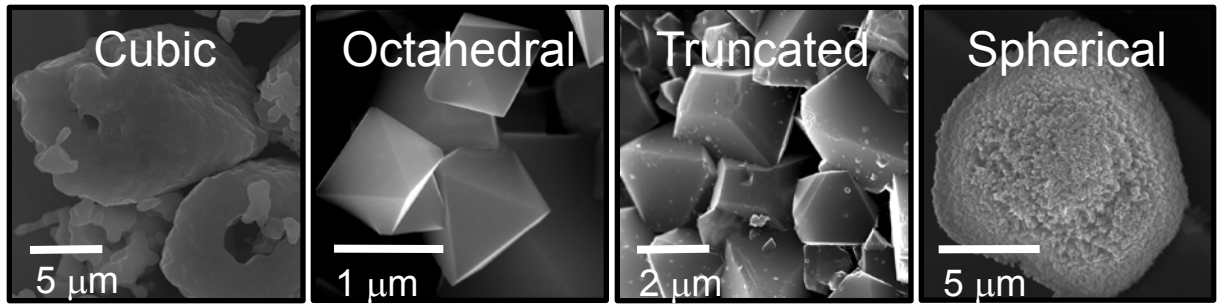


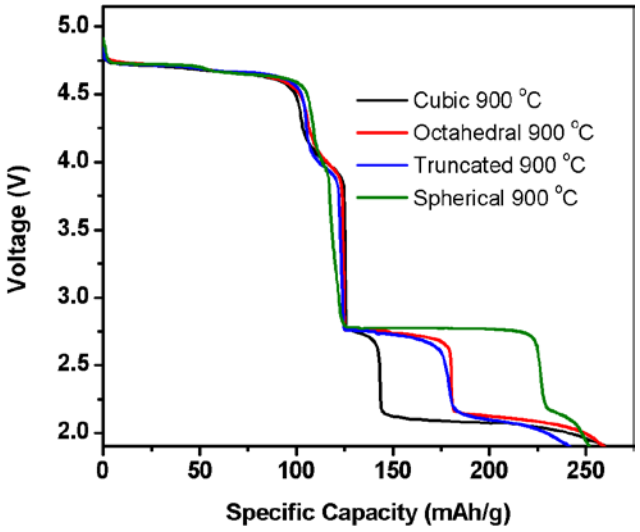


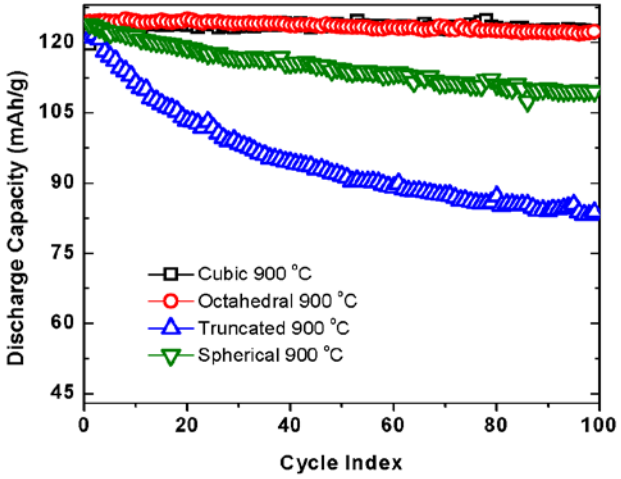
- Although Poly 1 annealed at 700 °C has a higher degree of cation ordering, it exhibits good electrochemical performance
- Truncated Poly 2 shows poor rate capability despite a highly disordered structure
- Morphology plays a dominant role in controlling the electrochemical performance

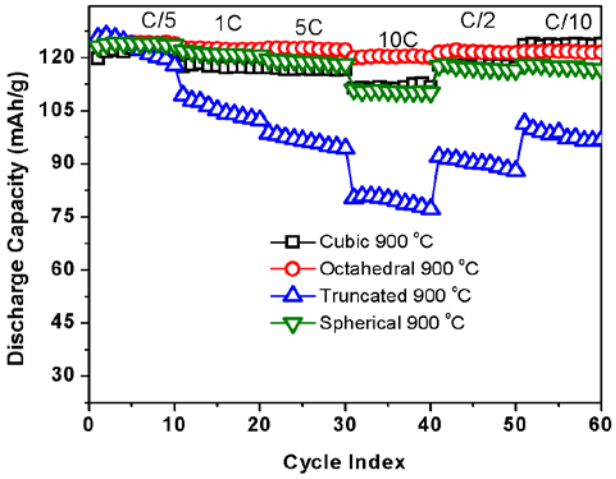
EXTENSION TO OTHER SYNTHESIS METHODS

Undoped $LiMn_{1.5}Ni_{0.5}O_4$ prepared by other synthesis techniques





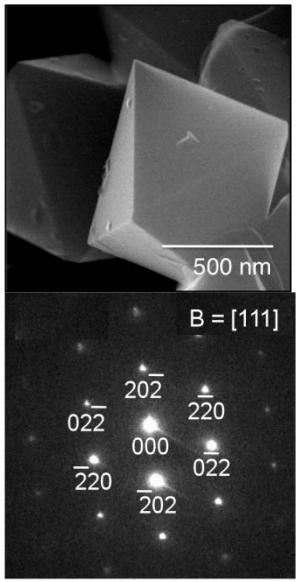




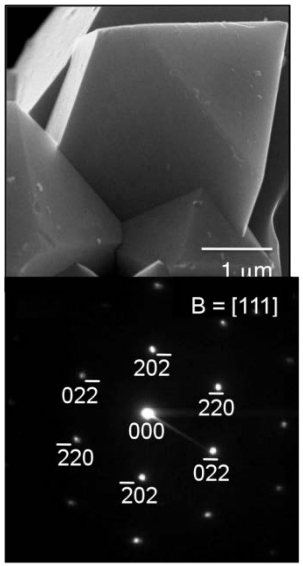
- Discharge profiles below 3 V indicate that both the Octahedral and Truncated Octahedral samples have the same degree of cation ordering, but differ significantly in electrochemical performance due to differences in morphology
- Morphology affects the electrochemical performance more profoundly compared to cation ordering

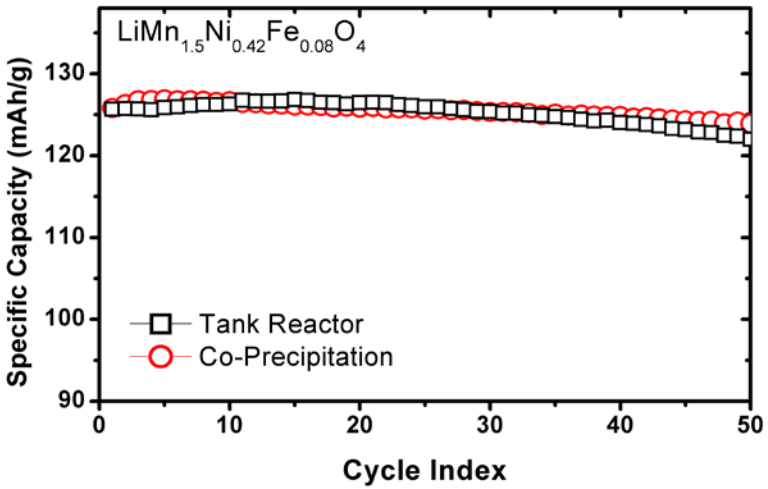
EXTENSION TO Fe-DOPED CATHODE MORPHOLOGY

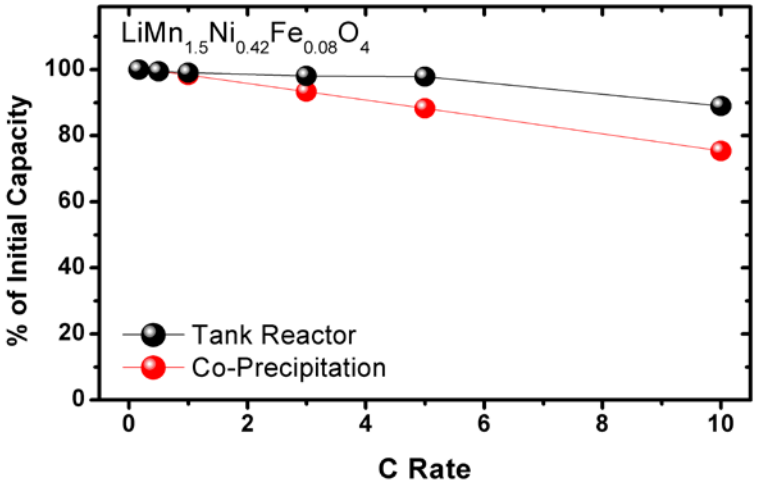
Tank reactor
$LiMn_{1.5}Ni_{0.42}Fe_{0.08}O_4$



Burette co-precipitation
$LiMn_{1.5}Ni_{0.42}Fe_{0.08}O_4$

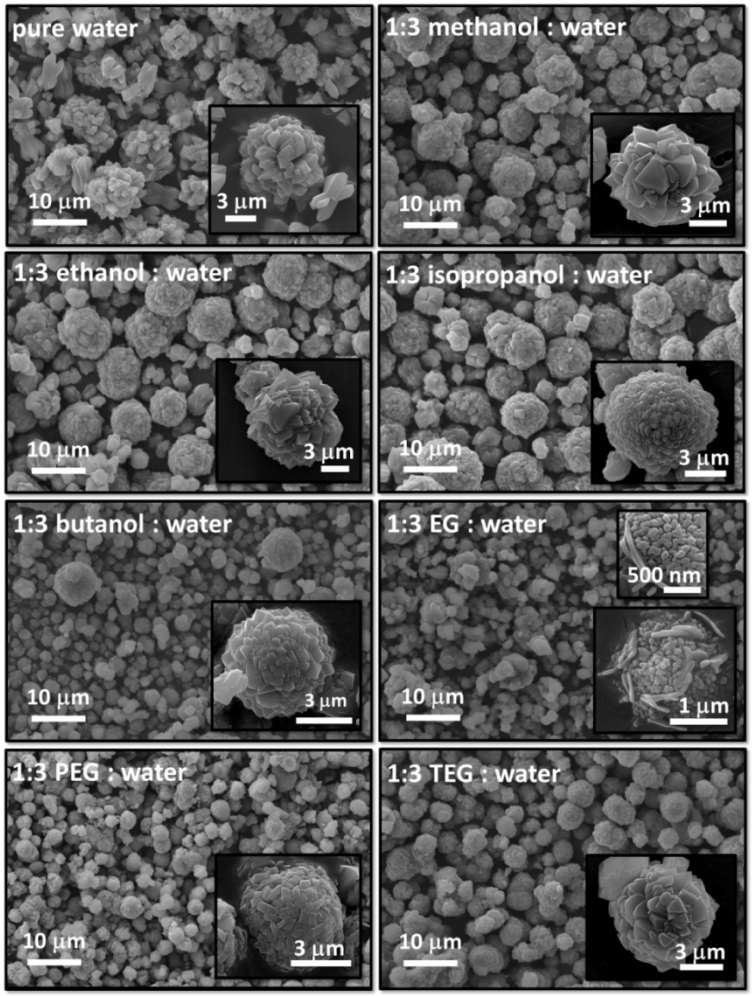


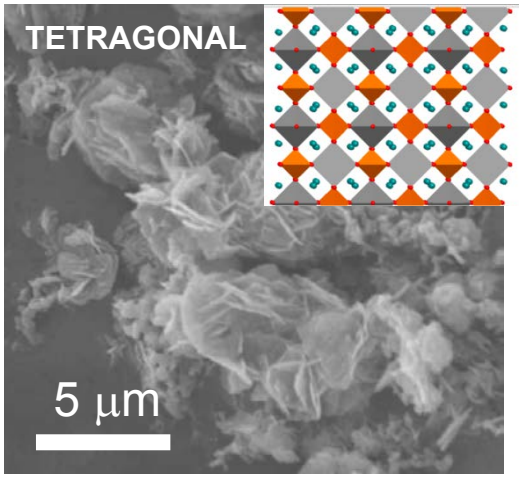


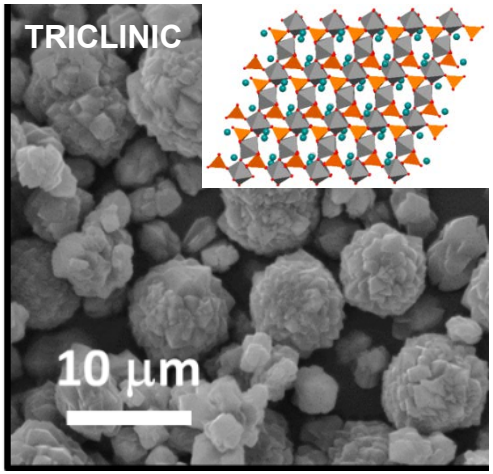


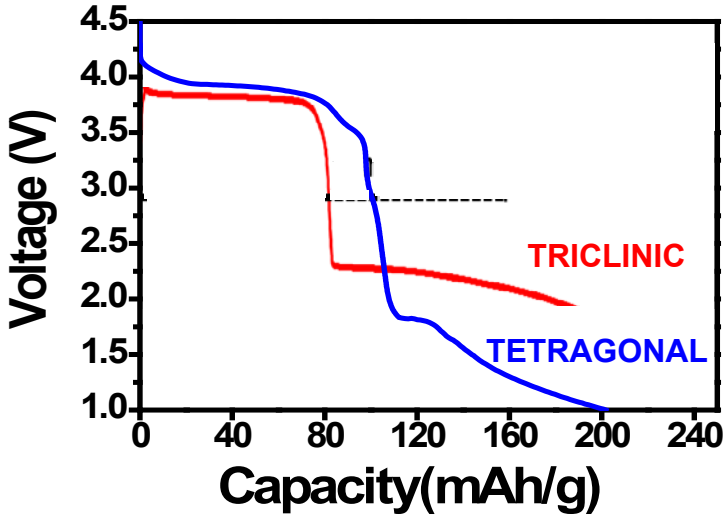
- Fe-doped samples made by both synthesis routes show octahedral morphology with {111} family of planes on the surface, unlike the undoped sample, resulting in high-performance for both the samples
- Segregation of Fe^{3+} to the surface may stabilize the growth of lowest-energy surfaces

MICROWAVE SYNTHESIS OF $LiVOPO_4$ POLYMORPHS



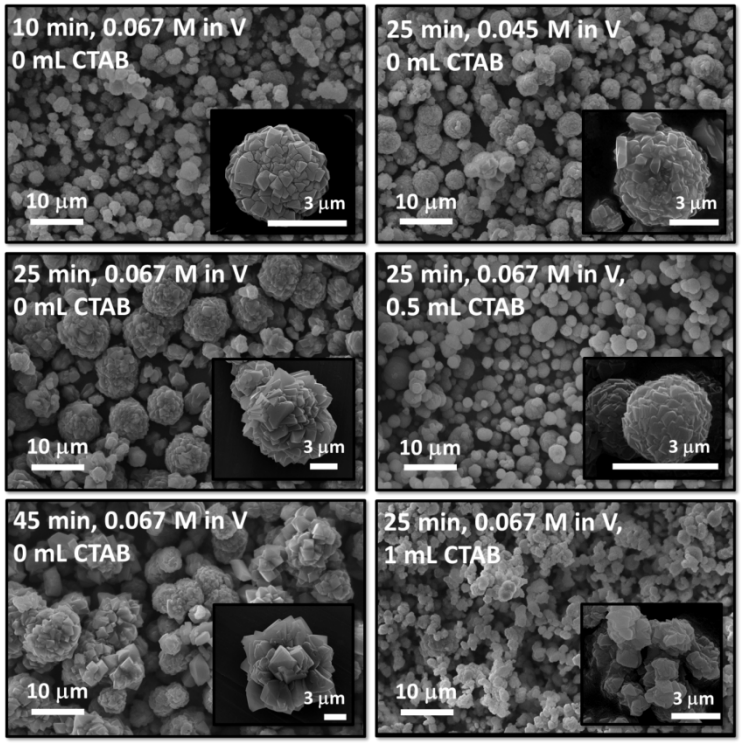




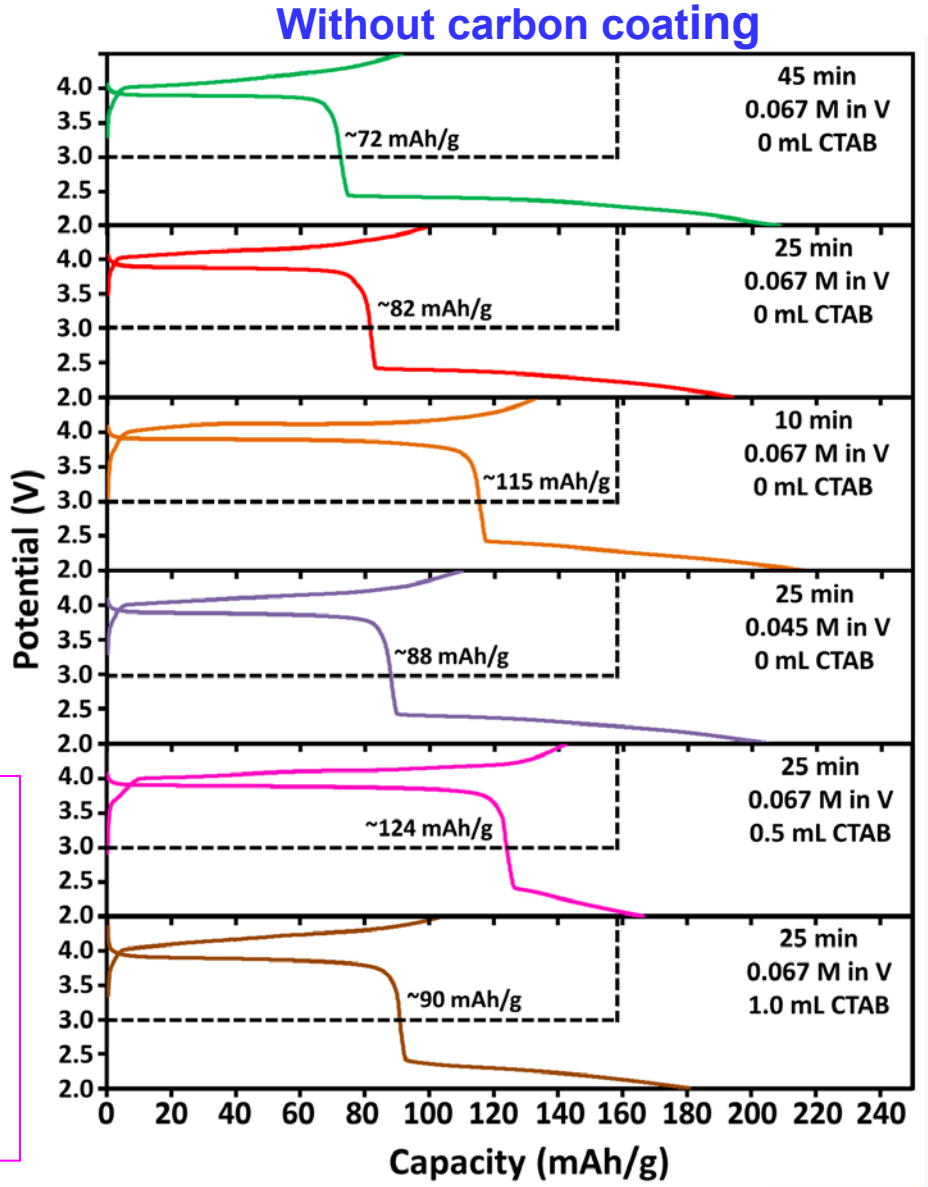


- All three polymorphs (tetragonal, orthorhombic, and triclinic) of $LiVOPO_4$ have been synthesized by employing mixed solvents and adjusting reaction conditions
- Discharge profile for second lithium insertion depends on the structure

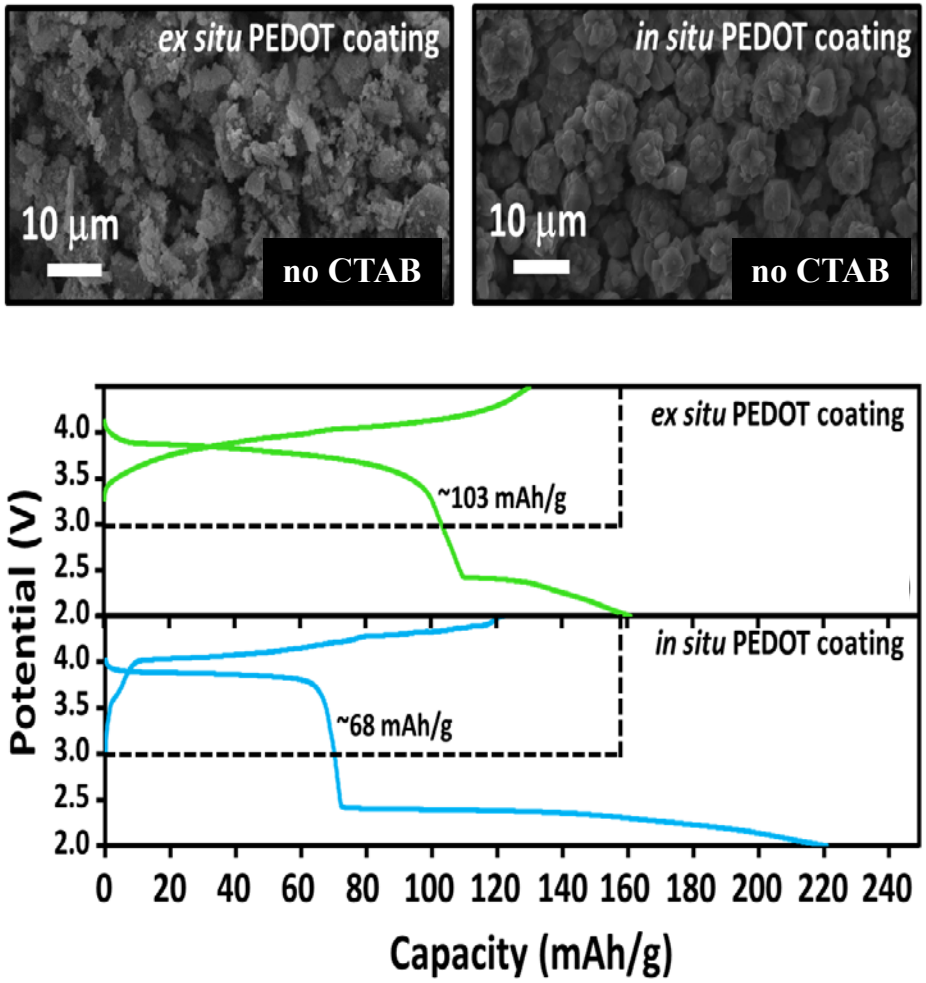
TRICLINIC $LiVOPO_4$



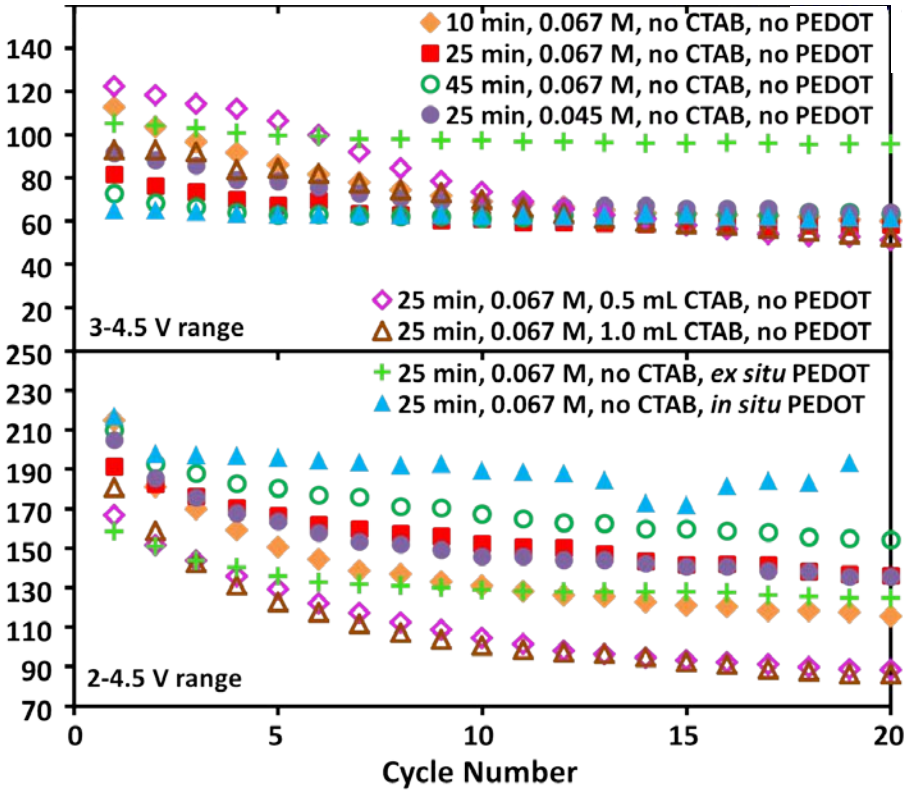
- Particle size decreases with shorter reaction time, lower precursor concentration, and increasing CTAB concentration
- Higher capacity was achieved in 3.0 – 4.5 V range with smaller particles



ROLE OF CONDUCTIVE PEDOT COATING ON $LiVOPO_4$

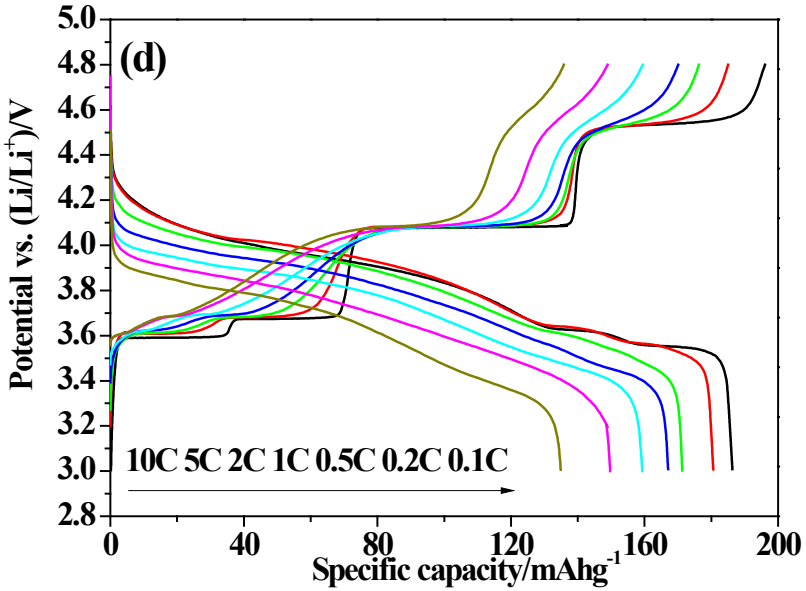


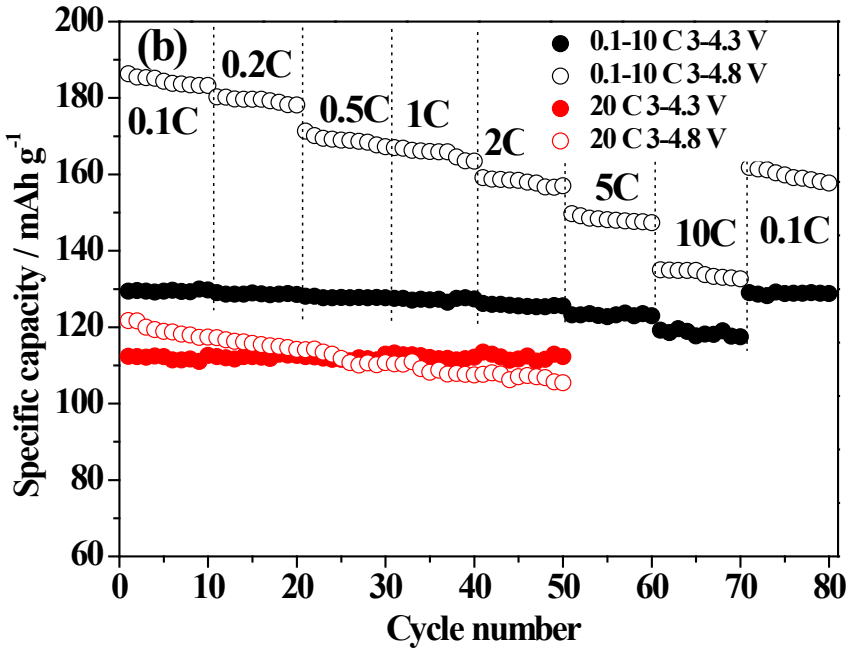
Triclinic $LiVOPO_4$

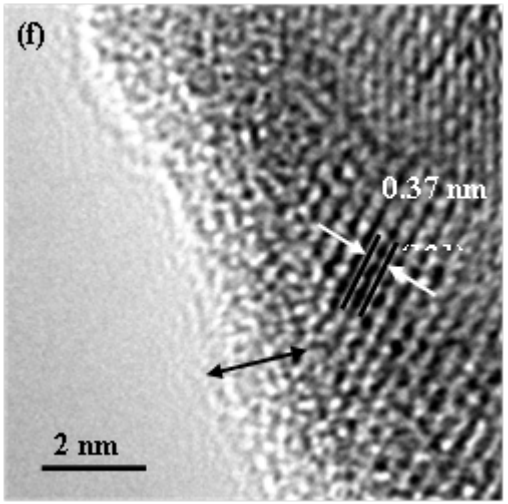


- *In situ* PEDOT coating increases the capacity corresponding to the second lithium insertion and improves the cyclability with capacities of ~ 200 mAh/g

SOLVOTHERMAL SYNTHESIS OF $Li_3V_2(PO_4)_3$-GRAPHENE

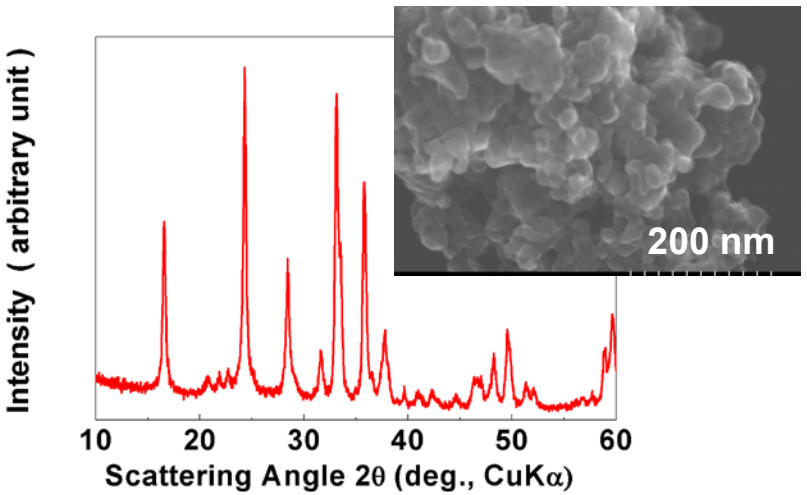


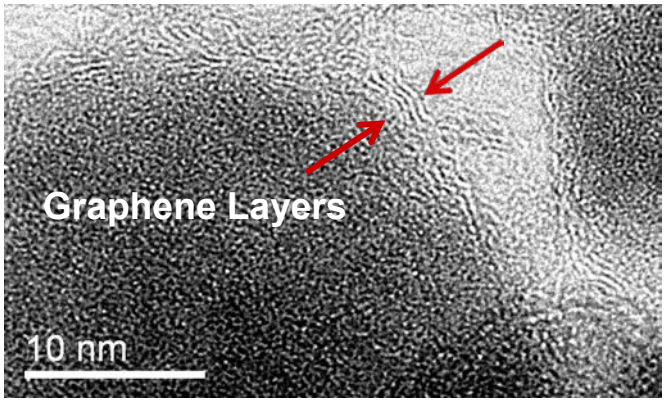


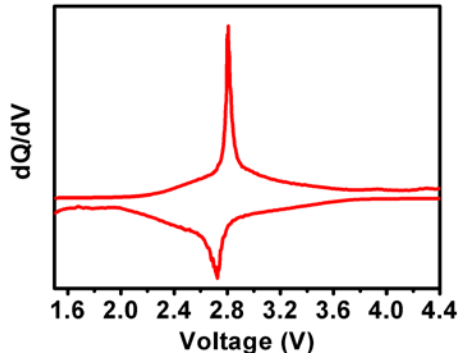


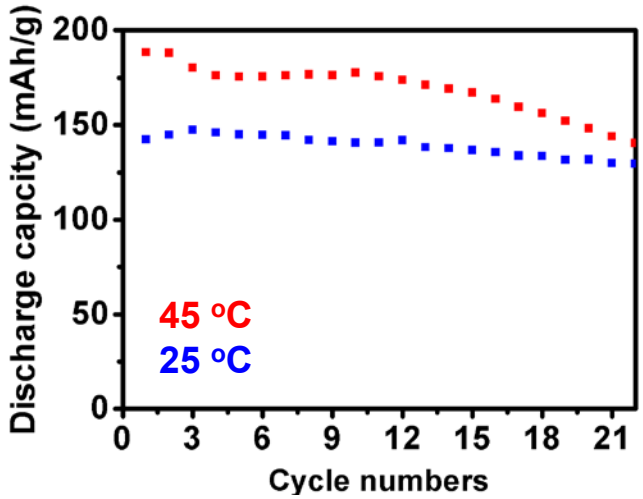
- $Li_3V_2(PO_4)_3$ supported on reduced graphite oxide was synthesized in a single step by a solvothermal process; the resulting sample was then coated with carbon with sucrose at higher temperatures
- The sample exhibits high capacities of close to 200 mAh/g and good rate capability

MICROWAVE SYNTHESIS OF Li_2FeSiO_4-GRAPHENE COMPOSITE









- Li_2FeSiO_4-graphene nanocomposite was synthesized in a single step by a microwave-assisted solvothermal process, followed by heat treatment
- The nanocomposite demonstrates the extraction of more than one lithium per Fe at higher temperatures

COLLABORATION AND COORDINATION WITH OTHER INSTITUTIONS

- University of Rhode Island – Professor Brett Lucht
  - *Investigation of SEI layer formation with stabilized 4.7 V spinel cathodes*

- Pacific Northwest National Laboratory – Dr. Jiguang (Jason) Zhang
  - *Discussion and coordination of results on 4.7 V spinel cathodes*
  - *Investigation of the 4.7 V spinel cathodes by solid state NMR*

- Hydro-Quebec – Dr. Karim Zaghib
  - *Discussion and coordination of results on 4.7 V spinel cathodes*

- Oak Ridge National Laboratory – Dr. Craig Bridges
  - *Investigation of the phosphate and 4.7 V spinel cathodes by spallation neutron source*

- DuPont – Dr. George Kodokian
  - *Evaluation of the 4.7 V spinel cathodes with DuPont's electrolytes*

PROPOSED FUTURE WORK

- Develop an understanding of the factors influencing the electrochemical performances of 5 V spinel cathodes, *e.g.*, role of cation doping and synthesis conditions on morphology and the influences of surface facets vs. cation ordering
- After further optimizing the synthesis conditions for all the three polymorphic modifications of $LiVOPO_4$, explore single-step synthesis of $LiVOPO_4$-graphene by microwave-assisted solvothermal process since is difficult to coat it with carbon under reducing atmospheres at elevated temperatures
- Optimize the microwave-assisted solvothermal synthesis conditions for Li_2MSiO_4-graphene (M = Mn, Fe, and Co) nanocomposites and their solid solutions as well as $Li_3V_2(PO_4)_3$-graphene nanocomposites to maximize the capacity and rate capability
- Explore the synthesis of $Li_2MP_2O_7$ (M = Fe, Mn, Co, and Ni) and $Li_9V_3(P_2O_7)_3(PO_4)_2$ and their composites with graphene by microwave-assisted solvothermal process
- Assess the surface structure of $Li_2M_{1-x}Fe_xSiO_4$ and $Li_2M_{1-x}Fe_xP_2O_7$ to see whether segregation of certain ions like Fe^{2+} occurs to the surface and thereby offers a better electrode-electrolyte interface and electrochemical performance

SUMMARY

4.7 V Spinel $LiMn_{1.5}Ni_{0.5}O_4$ cathode

- A systematic investigation of the various factors influencing the electrochemical properties of the high-voltage spinel reveals that particle morphology and surface facets play a dominant role compared to other factors such as cation ordering; certain cationic doping stabilizes preferentially the high-performance facets

- Two new methods (magnetic and discharge profile behavior below 3 V) have been developed to determine the relative degree of cation ordering in 4.7 V spinel

Polyanion cathodes

- All three polymorphic modifications of $LiVOPO_4$ have been synthesized by a microwave-assisted solvothermal process in mixed solvents; reversible insertion/extraction of more than one lithium has been demonstrated; coating with conductive agents like PEDOT without carbon coating enhances the performance

- $Li_3V_2(PO_4)_3$-graphene nanocomposite has been synthesized in a single step by a solvothermal process and shown to exhibit capacities close to 200 mAh/g

- Li_2FeSiO_4-graphene nanocomposite has been synthesized in a single step by a microwave-assisted solvothermal process and shown to exhibit reversible extraction of more than one lithium at 45 ^oC